

Mitigating Intergranular Attack and Growth in Lead-Acid Battery Electrodes for Extended Cycle and Operating Life

E.M. LEHOCKEY, G. PALUMBO, P. LIN, and A. BRENNENSTUHL

Deterioration in the performance of lead acid batteries is primarily governed by weight loss and growth of the positive electrodes, arising from creep and intergranular corrosion/cracking. The present investigation examines the impact of increasing the frequency of grain boundaries having low- Σ misorientations ($\Sigma \leq 29$), described by the Coincident Site Lattice (CSL) model, which are known to be resistant to these intergranular degradation phenomena. Electrode microstructures of various PbCaSn alloys processed to contain frequencies of special boundaries (in excess of 50 pct) exhibited reductions in weight loss of between 26 and 46 pct accompanied by declines in grid growth of between 41 and 72 pct. Moreover, the distribution of intergranular attack/cracking in the microstructure of these alloys can be predicted on the basis of the frequency of low- Σ special boundaries and grain size. In general, improvements in corrosion and creep/cracking occur without compromising tensile properties such as yield strength, ultimate tensile strength (UTS), and ductility. Modifying the crystallographic structure of grain boundaries in Pb alloy battery electrodes, thus, provides an opportunity for minimizing grid thicknesses (weight) and, hence, material costs in battery production, or for maximizing energy densities (Wh/kg) and cycle life performance.

I. INTRODUCTION

OPERATING and cycle lifetimes of conventional Pb-acid batteries are limited by the resistance of the positive electrodes (grids) to intergranular corrosion, cracking, and creep.^[1,2] Grid weight loss occurs when individual grains are removed from the electrode cross section as their surrounding boundaries are breached by intergranular corrosion/cracking. Alternatively, growth of the positive grid arises from the synergistic effect between creep and intergranular cracking. Dimensional changes occur in the electrode over time, causing adjacent plates to short, resulting in loss of capacity.^[2] Creep, at the low stresses and relatively high temperatures to which the electrodes are exposed, originates primarily from grain boundary sliding.^[4] Therefore, as “under-hood” temperatures in modern vehicles increase above $0.6 T_m$, growth is becoming the predominant factor in determining operating life in automotive Starter Lights Ignition (SLI) applications.^[5,6]

Battery electrodes were originally cast from lead antimony (PbSb) alloys. While these alloys offer excellent cycling capacity, mechanical strength, uniform corrosion rates, and fluidity for casting, they typically suffer from “plate-back” effects where antimony from the positive electrode deposits onto the negative grid during successive charge-discharge cycles.^[3] Antimony also reduces the hydrogen evolution voltage, promoting the formation of H_2 gas and accompanying water losses during charging.^[3] Hence, the prevalence of PbCaSn alloys, which eliminate plate-back and water losses, have increased in recent years with the popularity of valve-regulated (maintenance-free) battery designs in telecommunications, traction, and SLI applications. At the same time, however, PbCaSn grids are

more susceptible to weight loss, growth, and shedding of active material than their Sb-based counterpart.^[3]

Efforts to minimize the intergranular effects leading to weight loss and grid growth in PbCaSn alloys have traditionally focused on developing proprietary alloying recipes involving Ag, Se, As, *etc.*, which can degrade internal resistivity performance.^[7] Alloying additions have also been used as nucleants in order to refine grain size, producing some improvement in weight loss, although often at the expense of grid growth.^[2] An attempt to alter grain boundary structure, which offers the potential for *simultaneously* improving weight loss *and* grid growth, has never before been pursued. Grain boundaries having misorientation relationships which are crystallographically described by low Σ values in the Coincident Site Lattice (CSL) model are recognized to exhibit “special” properties, including increased resistance to diffusion,^[8] corrosion,^[9] cracking,^[10] and sliding and cavitation (creep),^[11,12] relative to “general” or “random” boundaries. Special properties associated with CSL interfaces having Σ values of less than 29 have been ascribed to their ordered structure and lower free volume compared with their random counterparts.^[13,14] A detailed review of the CSL model and the properties associated with low- Σ interfaces appears elsewhere in the literature.^[13,14]

Palumbo *et al.*^[15] demonstrated that the probability of arresting intergranular crack propagation (X) within a given depth (L) is related to the frequency of special boundaries and average grain size (d) in the microstructure, according to the following equation:

$$(1 - X) = (1 - P)^{\frac{2L}{d}} \quad [1]$$

where

$$P = F_{sp}^2 + 2 [F_0 F_{sp} (1 - F_{sp})] \quad [2]$$

where

F_{sp} = frequency of special, low- Σ CSL boundaries; and

E.M. LEHOCKEY, Senior Scientist, G. PALUMBO and A. BRENNENSTUHL, Principal Scientists, and P. LIN, Scientist, are with Ontario Hydro Technologies, Toronto, ON, Canada M8Z 5S4.

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Table I. Common Pb Alloys Used in Various Lead-Acid Battery Applications

Alloy	Application	Composition (Wt Pct)				
		Pb	Ca	Sn	Ag	Sb
PbSb	stationary	bal	—	—	—	1.7
PbCaSn	deep cycling	bal	0.6	1.0	—	—
“Hi” Sn	SLI*	bal	0.06	1.7	—	—
Pb-Ag	SLI	bal	0.03	0.6	0.03	—

*Starter lights ignition (automotive).

Static Corrosion Cell

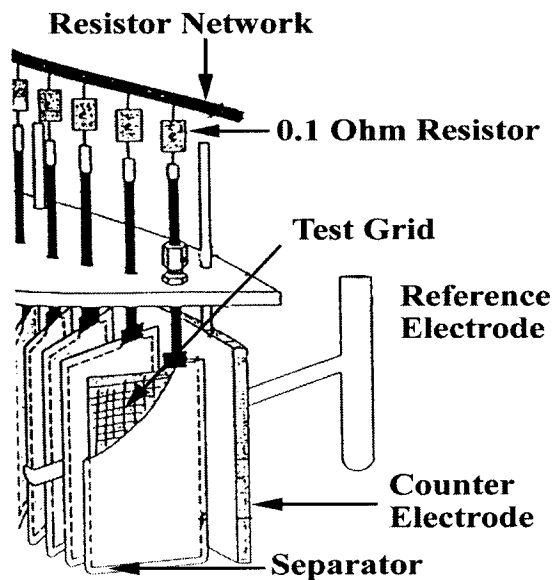


Fig. 1—Schematic diagram of static corrosion cell.

F_0 = frequency of boundaries unfavorably oriented to the stress axis.

This model implies that crack propagation, which may play a dominant role in grid growth, can be significantly curtailed in microstructures having high frequencies of low- Σ CSL boundaries. Recently, the authors have demonstrated that the frequency of low- Σ CSL boundaries can be enhanced in *pure* lead, from the levels of 10 to 12 pct found in cast material to values in excess of 50 to 70 pct, by a proprietary metallurgical processing protocol.^[16] It was further demonstrated that such modifications in the structure of grain boundaries in *pure* lead substantially increases its creep resistance, upon which the growth rates of battery electrodes depend.^[2,17] The intention of the present work is to quantify the impact of elevating the frequency of special boundaries in various *commercial* lead alloys on the mechanical, corrosion, and growth properties relevant to battery electrode (grid) performance, fabrication, and reliability.

II. EXPERIMENTAL

A. Materials Preparation and Characterization

Rectangular coupons (measuring $4 \times 10 \times 0.3$ cm) of various Pb alloys, having the compositions listed in Table

I, were strip-cast by Cominco Ltd. (Mississauga, ON). Alloy compositions were selected to represent a cross section of those found in SLI, “deep-cycling,” stationary, and traction applications. A proportion of the “as-cast” samples of each alloy were grain boundary engineered (GBE*) using

*GBE is a trademark of Ontario Hydro, 700 University Ave., Toronto, Ontario, Canada.

a patented process developed to elevate the frequency of CSL grain boundaries in the range of $1 \leq \Sigma \leq 29$.^[16] The grain boundary character distribution (GBCD) in the cast and processed material was characterized using a JEOL**

**JEOL is a trademark of Japan Electron Optics Ltd., Tokyo.

840 scanning electron microscope equipped with orientation imaging microscopy (OIM). Misorientations between adjacent grains are calculated from changes in the electron backscatter pattern as the incident beam “steps” in discrete intervals across the raster area.^[18] Grain boundaries were classified according to Brandon’s criterion^[19] for the maximum permissible deviation ($\Delta\theta$) from exact coincidence, according to the following equation:

$$\Delta\theta \leq 15 \text{ deg } \Sigma^{-1/2} \quad [3]$$

A complete description of the OIM technique, its merits, and limitations, is available in the literature.^[18] The frequency distribution of CSL boundaries for $3 \leq \Sigma \leq 29$ and grain size were determined and compared between materials in the “processed” vs “as-received/cast” condition. Changes in the distribution of CSL boundaries were also monitored, with prolonged exposure to temperatures of 90 °C ($0.6 T_m$) for a period of 1 month, to ensure adequate thermal stability of the GBCD under the most severe conditions likely to be encountered in service.

B. Corrosion Tests

Differences in corrosion (weight loss) and growth performance between cast and GBE-processed materials were evaluated using standard static polarization and cycling tests accepted by the battery industry to simulate performance under float and deep-discharge conditions.^[20–23] Miniature (5×10 cm) battery grids were prepared from cast and GBE-processed material by an expansion technique consistent with production practices. A solid lead alloy strip material is pierced by an array of rotating knives and expanded in the traverse direction into a diamond lattice geometry, forming a mesh.^[20]

All grid electrodes were weighed to the nearest milligram and immersed in a corrosion cell containing a solution of 1.28 sg (specific gravity) H_2SO_4 at 70 °C, as illustrated in Figure 1. Test grids (working electrodes) are arranged in a radial direction in the cell, as shown, surrounded by a pure lead counter electrode along the circumference of the cell, which also extends radially (not shown) between the individual working electrodes to enhance uniformity in over-potential across the grids. Working electrodes were polarized using a 200 mV overpotential (Hg/HgSO₄ reference electrode) for periods of less than or equal to 35 days. In separate tests, grids were also pasted with PbO₂ (active material) and assembled into individual battery cells. Cells were cycled between 0 and 1.71 V d.c. across the

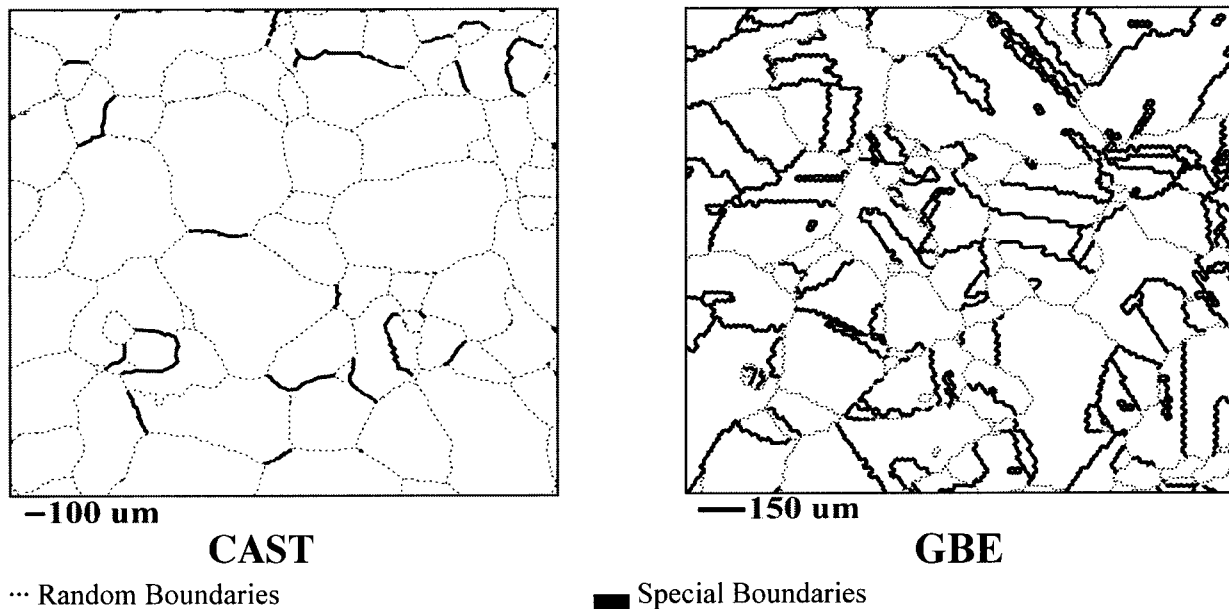


Fig. 2—Schematic OIM images comparing the distribution of special boundaries in the Cast and GBE PbCaSn alloy.

Table II. Grain Boundary Statistics for As-Cast and Optimized GBE Microstructures in PbCaSn and PbCaSnAg Battery Grid Alloys

Boundary Type	PbSb		PbCaSn		PbCaSn Ag		“Hi”Sn	
	Cast	GBE	Cast	GBE	Cast	GBE	Cast	GBE
$\Sigma 1$, pct	3.5	6.5	8.5	10.7	14.5	3.4	8.4	5.4
$\Sigma 3$, pct	7.6	42.2	5.5	34.2	0.4	55.1	3.0	56.4
$\Sigma 9 + \Sigma 27$, pct	3.2	5.4	0.5	9.5	1.0	9.7	1.7	12.2
Other CSLs $\Sigma \leq 29$, pct	2.2	4.4	6.0	13.0	5.6	2.7	8.8	2.3
$3 \leq \Sigma \leq 29$, pct	13.0	52.0	11.9	51.0	7.0	67.6	13.5	70.9
Random	83.5	41.5	79.6	43.3	78.5	29.0	78.1	23.7
Average Grain size, μm	34.2	25.4	42.6	17.6	121.9	14.6	98.9	19.8

PbSO₄/PbO₂ corrosion potential at a rate of 2 cycles/day for 35 days. Conventionally cast and GBE-processed grids were removed periodically from each experiment, cleaned in a “stripping” solution (10:2:1) NaOH:manitol:hydrazine dihydrochloride in 1 L of water, and subsequently reweighed to establish mass loss. Grids were digitally scanned and compared before and after corrosion testing for changes in overall electrode area accrued from growth. Mass loss and growth data were based upon the average of measurements on two replicate grids removed at each interval. High-resolution digital images, along with metallographically prepared cross sections of the conventional and GBE grids, were examined to study the depth distribution of intergranular cracking/attack.

C. Mechanical Testing

ASTM Type V dogbones were prepared from strips of cast and GBE material and tensile tested according to ASTM E8, using a strain rate of 5 mm/min, to determine the effect of the GBCD on yield strength, ultimate tensile strength (UTS), and ductility (ϵ_{break}).^[24] Tensile tests were subsequently repeated at 24 hours and 10 days after material fabrication to establish the impact of low- Σ CSL grain boundary content on room-temperature age hardening/embrittlement. In all cases, a minimum of five replicate

samples of each material were tested to define confidence intervals associated with the mechanical properties of interest.

III. RESULTS AND DISCUSSION

A. Mesotexture/Grain Boundary Characterization

Orientation images illustrating the effect of processing on the grain boundary structure of the PbCaSn alloy are presented in Figure 2. Solid lines delineate twin and other special boundaries, while dotted lines represent random boundaries. The frequency of special boundaries was increased, by suitable processing, from approximately 12 to 51 pct. Corresponding increases in the fraction of low- Σ CSL boundaries among the four alloys considered are summarized in Table II. Particularly high special boundary frequencies, in excess of 68 to 70 pct, were achieved in the most popular PbCa“Hi”Sn and PbCaSnAg alloys currently used by many of the larger battery manufacturers, as summarized in Table II. Contributions from low-angle boundaries (*i.e.*, $\Sigma 1$) were neglected in all analyses due to difficulties in distinguishing these interfaces from damage (dislocations) accumulated during sample preparation and handling. Therefore, the percentage of special grain bound-

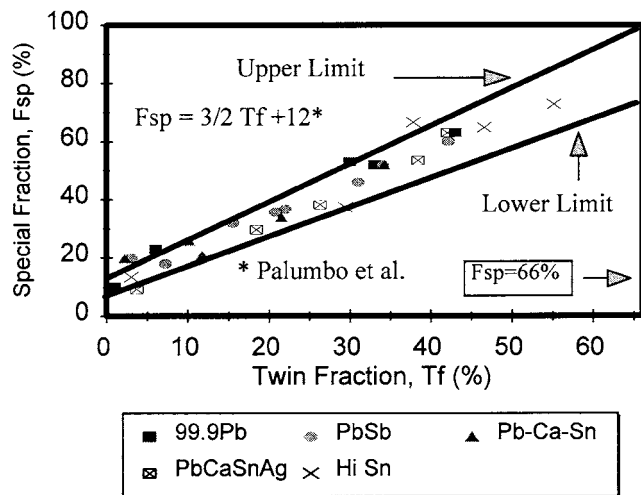


Fig. 3—Correlation between proportion of twinning and special grain boundaries in the microstructure among lead and its alloys.

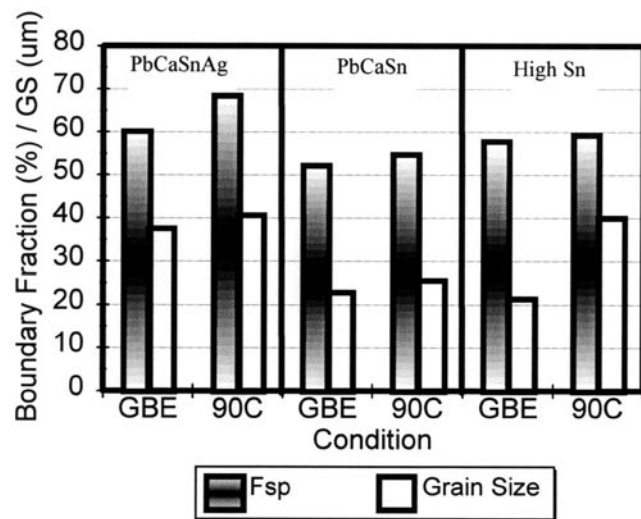


Fig. 4—Variation in grain boundary character distribution and grain size of PbCaSn alloys with exposure to elevated temperature.

aries quoted may be marginally skewed toward lower values than are actually present in the microstructure.

Clearly, the propensity for special boundary formation in these alloys is sensitive to alloy composition, reflecting the role of solutes in enhancing or suppressing the thermodynamic stability of these interfaces, as previously reported in the literature.^[13] Increases in the proportion of low- Σ CSL boundaries in all of the fcc alloys are derived primarily from the proliferation of twins ($\Sigma 3$) and their crystallographically related variants $\Sigma 3^n$ (*i.e.*, $n = 1, 2, 3$, etc.). Figure 3 shows the correlation between the frequency of special boundaries and twins in the microstructure among the four alloys and pure lead. Results generally fall between the upper and lower bounds proposed by Palumbo *et al.*^[25] The upper bound assumes that each twin adds one additional special boundary to the microstructure, on the basis that twins lower the energy of contacting boundaries according to the Fullman-Fisher concept,^[26] while the lower limit assumes that the special boundary fraction only increases by the addition of the twin itself.^[25] Table II clearly demonstrates that high frequencies of low- Σ , special bound-



Fig. 5—Comparison in the condition of the conventionally cast ($F_{sp} = 10$ pct) and GBE ($F_{sp} = 71$ pct) PbCa“Hi”Sn grids after 12 days in 1.28 sg in H_2SO_4 at 70 °C under static polarization using a 200 mV overpotential.

aries can be attained in a wide variety of commercially significant lead alloys used in battery manufacturing.

The GBCD and grain size in three PbCaSn GBE alloys are compared in Figure 4 before and after prolonged exposure to temperatures of 90 °C. The elevated temperatures to which batteries are often exposed neither promote excessive grain growth nor detrimentally affect the frequency of special grain boundaries in the microstructure. In impure/alloy materials, low- Σ , special boundaries are generally more prone to boundary migration than random boundaries, which are characterized by higher-order Σ relationships (*i.e.*, $\Sigma > 29$).^[27,28] In the present case, however, the microstructure exhibits sufficient thermal stability to ensure that the beneficial properties accrued from the introduction of special boundaries will be sustained under the most rigorous operating conditions.

B. Grid Growth and Corrosion

The appearance of GBE and conventional Pb-“Hi”Sn grids (having GBCDs similar to those represented in Table II) after 12 days of static corrosion testing are compared in Figure 5. Processed grids containing special grain boundary fractions in excess of 60 to 70 pct remain fully intact, while conventional grids experience a complete loss in structural integrity due to extensive through-wall cracking and grain dropping. Corresponding micrographs comparing the extent of grain dropping/crack penetration through the grid cross section appear in Figure 6. Approximately 0.25 mm, or one-half of the original 0.51-mm GBE grid thickness, remains uncompromised by cracking/grain dropping after 12 days of testing, while only 0.12 mm of the conventional material having the same initial thickness remains intact. Such improvements are attributed to the inherent resistance of special low- Σ boundaries to crack propagation and intergranular corrosion, analogous to results reported by Lin

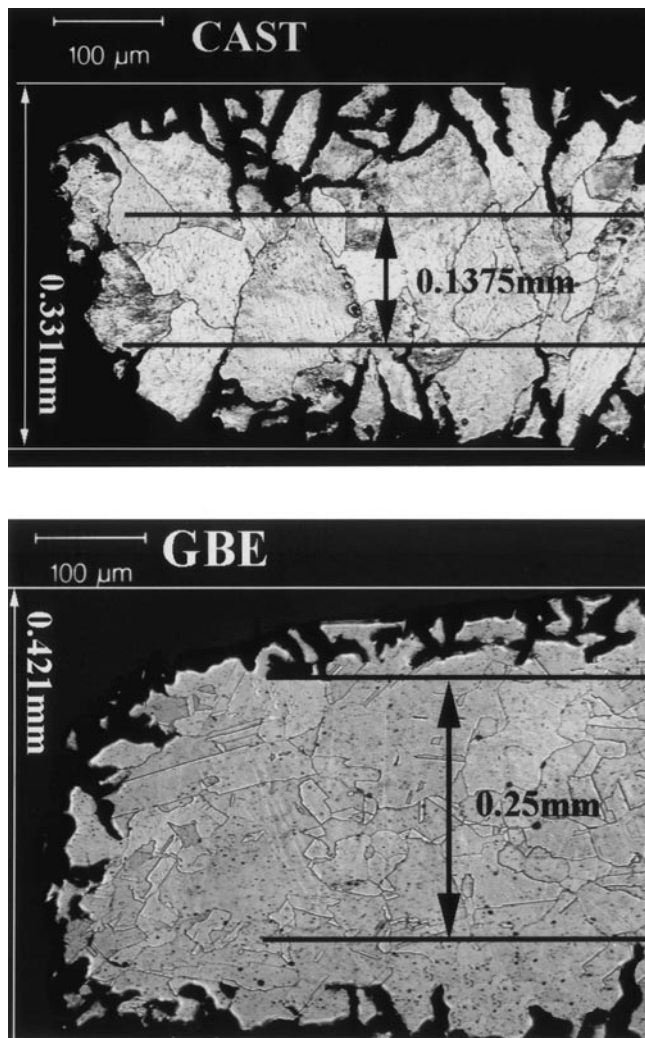


Fig. 6—Comparison in depth of intergranular attack/grain dropping through the cross section of conventional cast ($F_{sp} = 13$ pct) vs GBE ($F_{sp} = 63$ pct) PbCa“Hi”Sn grids in 70 °C, 1.28 sg H_2SO_4 after 12 days under 200 mV static polarization.

and Palumbo in ASTM G-28 corrosion testing of sensitized nickel alloys.^[9] The corresponding OIM image, detailing the GBCD surrounding a typical crack that has penetrated into the cross section of the “Hi”Sn grid during static corrosion testing, is presented in Figure 7. Twin ($\Sigma 3$) and other low- Σ boundaries for $\Sigma \leq 29$ are delineated by solid dark lines, while random boundaries (*i.e.*, $\Sigma > 29$) appear as dotted lines. Intergranular attack through the grid cross section is clearly confined to random boundaries. No instances of crack branching along twins or other low- Σ special boundaries intersecting the main crack are evident, substantiating the role of low- Σ special boundaries in resisting the intergranular attack/cracking responsible for weight loss and grid growth. This is consistent with previously reported preferential stress corrosion cracking along random boundaries in Ni alloys and intergranular fracture of β -brass.^[15,29,30]

Grid weight loss and growth as a function of time under polarization are shown in Figures 8(a) and (b), respectively, for PbCaSnAg alloys containing special boundary fractions of 7 pct (cast) vs 68 pct (GBE). Growth rates as a function of polarization time, measured in cast material of varying

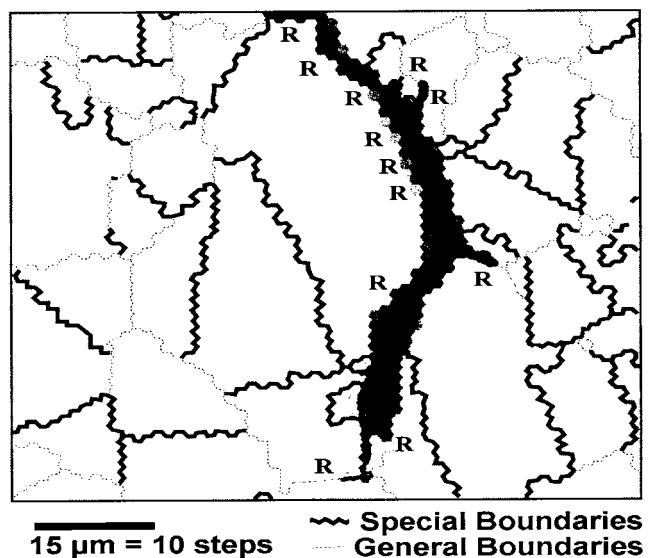
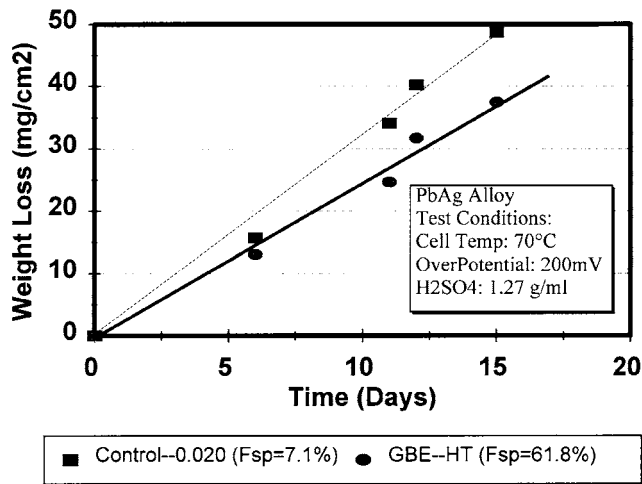


Fig. 7—OIM image detailing the GBCD surrounding a crack in the GBE Pb-Ag alloy after corrosion testing.

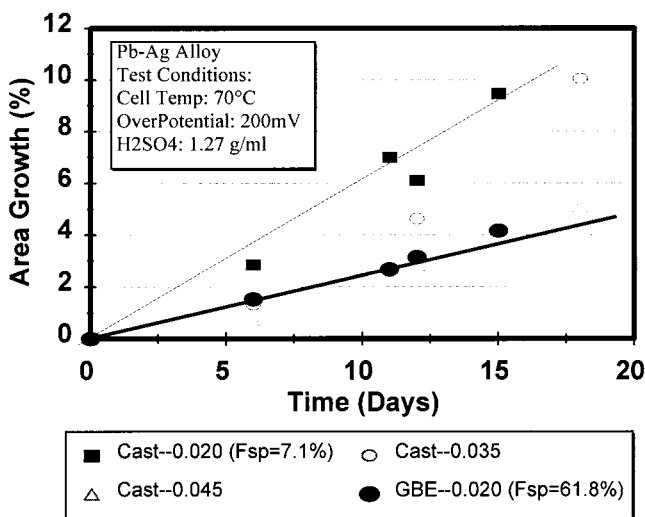
thickness from 0.51 to 1.14 mm, are also shown. Processing to elevate the special grain boundary fraction reduces the rate of weight loss and growth by 30 and 56 pct, respectively, relative to conventional cast material. Growth rates (Figure 8(b)) for GBE-processed grids having thicknesses of 0.51 mm are similar to those of conventional grids having twice this thickness (or 1.14 mm), suggesting the potential for reducing current grid thicknesses by 50 pct without compromising operating life.

Improvements in (a) weight loss and (b) grid growth under static corrosion and cycling conditions, achieved by enhancing the frequency of low- Σ CSL boundaries in the three PbCaSn alloys, are summarized in the bar graphs of Figure 9. Percentages shown reflect the reduction in growth/weight loss between the conventional (cast) and GBE-processed material. Typical weight loss and growth rates for *conventional* low-antimony (Pb 1.7Sb; Table I) grids of similar thickness are also shown for reference. The presence of special boundaries reduces weight loss in these alloys by 26 to 46 pct. Weight loss accumulated in the PbCaSn alloys under cycling conditions rivals that of the PbSb systems. Special boundaries appear to be more effective in reducing weight loss under cycling compared with static polarization conditions. This reflects a predominance for general attack under static corrosion conditions, which remains unaffected by local grain boundary structure. In contrast, cycling tends to favor localized, intergranular attack driven by oxide volume changes associated with excursions across the $PbO_2/PbSO_4$ potential during charge/discharge.^[1,2]

Low- Σ CSL boundaries appear to effect a greater impact on grid growth than weight loss. Growth rates are seen to decrease by 41 to 72 pct as special boundary fractions exceed 50 pct. Growth rates after processing are suppressed to levels consistent with those of conventional PbSb alloys. Growth rates among the three PbCaSn alloys exhibit a consistent correlation with the square of special boundary frequency (F_{sp} , in percent) and the inverse root of grain size (GS), as evidenced in Figure 10. As the special grain boundary frequency increases and/or grain sizes are refined,



(a)

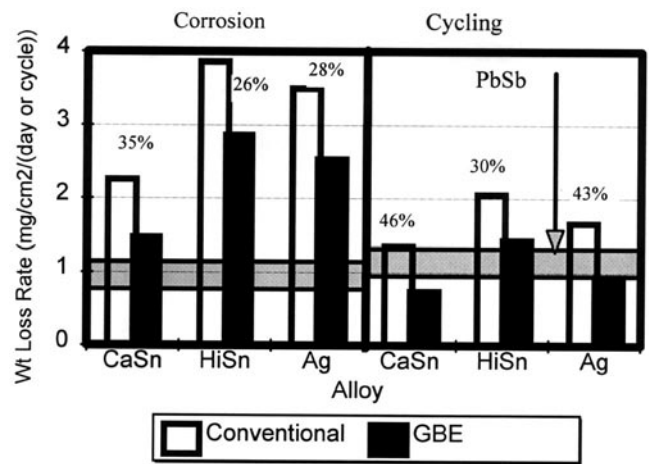


(b)

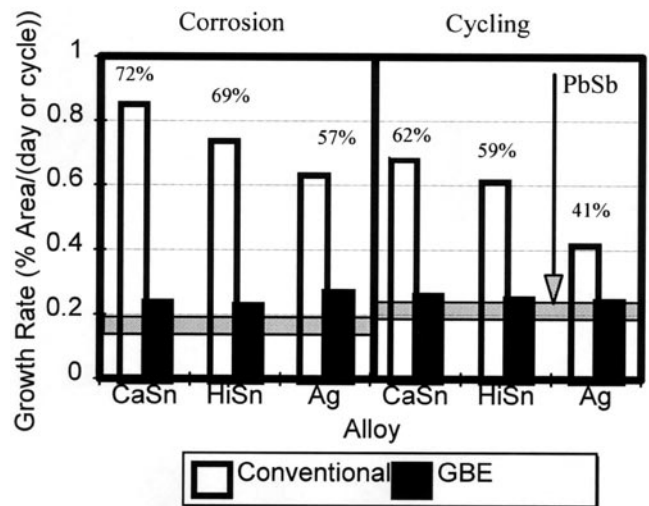
Fig. 8—Effect of processing on (a) weight loss and (b) grid growth in the Pb-Ag alloy.

growth rates experience an abrupt reduction as $F_{sp}^2/GS^{1/2}$ approaches approximately $500 \mu m^{-1/2}$. A reasonable correlation with the inverse of grain size advocates a significant contribution of cracking to growth, over the traditional view of growth as purely a creep phenomenon. Furthermore, attempts to formulate an empirical correlation directly with grain size (*i.e.*, growth $\propto GS^n$), indicative of a creep mechanism, proved unsuccessful.

Improvements in grid weight loss and growth rate translate into both cost and performance benefits. Figure 11 projects the increase in energy density (Wh/kg) and material cost savings per battery as a function of the percentage reduction in grid thickness. These calculations are based on a total battery grid weight of 18.1 kg (40 lbs), of which 2.7 kg (6 lbs) is comprised of grid material. A 50 pct reduction in grid thickness, demonstrated by Figure 9, would yield increases in energy density (Wh/kg) of 17 to 20 pct while decreasing material costs by \$1.50/battery (lead price = \$0.25/lb). Alternatively, at current grid thicknesses, improvements in growth of 50 to 75 pct derived from changes in the GBCD are expected to provide *at least* a two- to four-fold longer operating/cycle life over the 150 to 170



(a)



(b)

Fig. 9—Effect of increasing the frequency of special boundaries in the (a) weight loss and (b) growth resistance among the three PbCaSn alloys considered. Typical rates for conventional PbSb are shown for comparison. (Note: units of weight/growth for static and cycling tests are normalized against days and cycles, respectively.)

cycles normally achieved in present SLI batteries. Increasing energy density and cycle life are particularly critical in electric vehicle (EV) applications, translating directly into longer range and reduced replacement cost, respectively. Since batteries constitute a significant fraction of the weight and price of EVs, the effect of increasing energy density and/or cycle life on vehicle performance and maintenance costs cannot be overestimated. Such improvements in battery performance will be required if lead-acid systems are to compete with emerging technologies that are currently too expensive or unreliable (*e.g.*, NiMH and zinc-air).^[2,5]

C. Mechanical Properties

The affect of low- Σ CSL boundaries on the yield strength, UTS, and ductility (strain-at-break, ϵ_{break}) of the four alloys considered is shown in Table III. Increasing the content of low- Σ grain boundaries has no significant detrimental effect on either tensile strength or yield strength. Although a moderate decline in tensile strength of the

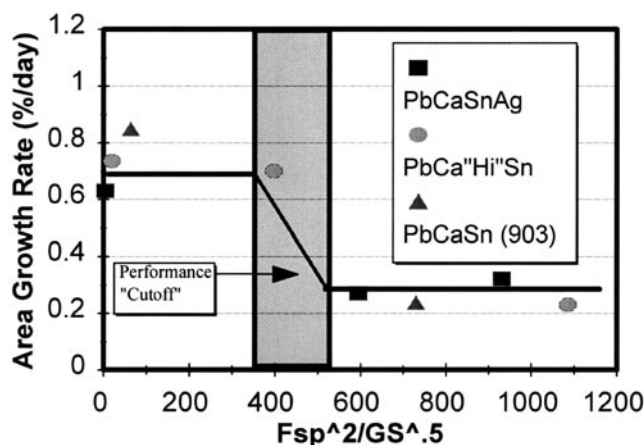


Fig. 10—Correlation of special boundary frequency (F_{sp}) and GS with growth rate among three PbCaSn grid alloys of various grain sizes (20 to 100 μm) and special boundary frequencies (10 to 70 pct).

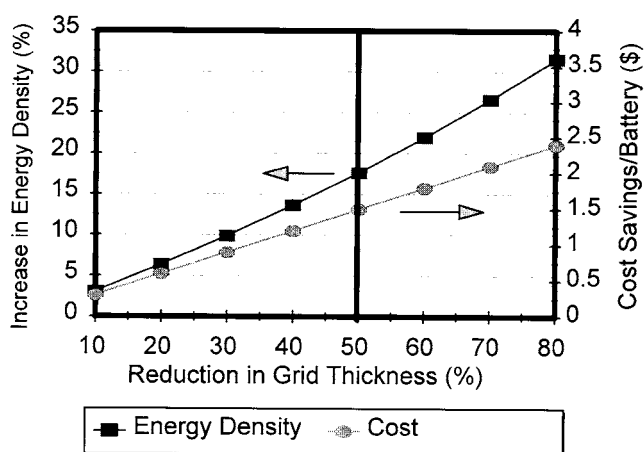


Fig. 11—Calculated improvements in energy density and material cost savings with reductions in grid thickness. (Calculations assume a typical 27 kg battery mass of which the grid accounts for 6 kg).

Table III. Effect of Special Grain Boundary Frequency on Yield Stress, UTS, and Strain-at-Break ϵ_b (Failure) of PbSb and PbCaSn Alloys

Alloy	Condition	Yield Stress (MPa)	UTS (MPa)	Strain-at-Break (Pct)
PbCaSn	cast	$21.4 \pm 5.0^*$	27.9 ± 6.5	6.2 ± 0.6
PbCaSn	GBE	16.7 ± 2.5	20.3 ± 5.6	12.4 ± 1.3
PbSb	cast	38.5 ± 2.5	43.5 ± 3.5	21.8 ± 2.5
PbSb	GBE	41.1 ± 3.0	43.2 ± 2.2	49.8 ± 3.5
PbCaSnAg	cast	28.2 ± 8.0	41.9 ± 3.5	2.6 ± 1.0
PbCaSnAg	GBE	21.1 ± 3.0	34.9 ± 5.0	7.9 ± 3.0
PbCa'Hi'Sn	cast	33.1 ± 4.0	44.2 ± 4.0	5.8 ± 1.2
PbCa'Hi'Sn	GBE	36.5 ± 6.0	64.0 ± 6.0	21.7 ± 2.4

*Error estimates given for the 95 pct confidence interval.

PbCaSn alloy was noted, the residual strength of the processed material, being greater than 13 to 15 MPa (~ 2000 psi), is sufficient to ensure that the mechanical integrity of the grids is not jeopardized during forming, handling, and cell assembly operations. At the same time, all alloys undergo an increase in ductility. Strain-at-break consistently increases by a factor of 2 to 3 in alloys having special

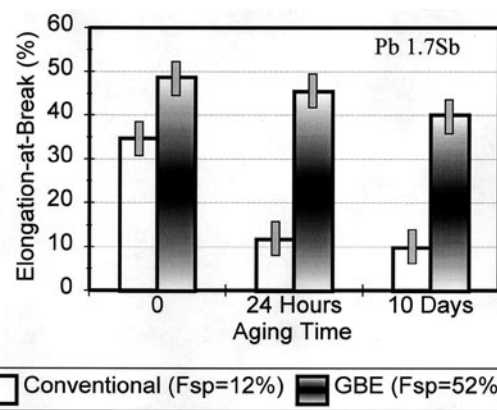


Fig. 12—Effect of special grain boundaries on the age-hardening embrittlement susceptibility of a PbSb alloy.

boundary fractions in excess of 50 pct relative to the conventional cast material. Enhanced ductility is of significant benefit in minimizing the number of defects caused by the high deformations applied to the material during grid expansion processes, in which an open lattice mesh is formed from a solid strip. Therefore, the improvements in corrosion and growth demonstrated in Section III-B are not obtained at the expense of the mechanical properties necessary for grid forming and production.

The absence of an increase in yield strength/UTS, despite grain size refinement (Table III) and the improvement in ductility arising from the increase in special boundary frequency, is not unexpected. The enhanced structural order of low- Σ special boundaries reduces their interaction with glissile dislocations, which minimizes dislocation pileups from which Hall-Petch-type strengthening originates.^[11,12] At the same time, as a by-product of introducing low- Σ CSL boundaries into the microstructure, significant grain size refinement can be effected to promote ductility (Table III) without jeopardizing the growth (creep/cracking) characteristics (Figure 9) that would normally restrict grain sizes to those found in the as-cast material (≈ 50 to 100 μm).

Many strip-cast Pb alloys from which grids are manufactured tend to age harden. Alloys are rapidly cooled from the melt, quenching solutes into solid solution. Hardening during subsequent exposure to room temperature ($>0.5 T_m$) renders the alloys susceptible to cracking during expansion, handling, and cell assembly. Variations in the strain-at-break of a PbSb alloy having a special boundary frequency of 10 pct (cast) vs 60 pct (GBE) are compared, over a 10-day period at room temperature, in Figure 12. The error bars delineate 95-pct confidence intervals. Ductility of the conventional cast alloy is reduced from 35 to 10 pct, while microstructures containing fractions of low- Σ CSL boundaries in excess of 50 pct do not experience any statistically significant time-dependent embrittlement. Moreover, the strain-at-break measured in the GBE material after 10 days of aging remains higher ($\epsilon_b \approx 40$ pct) than that of the conventional material immediately after casting. Hence, the presence of low- Σ CSL boundaries not only improves ductility, but provide measurable resistance to age hardening. Similar trends indicating the role of special boundaries in suppressing age hardening were observed in selected PbCaSn alloy systems.

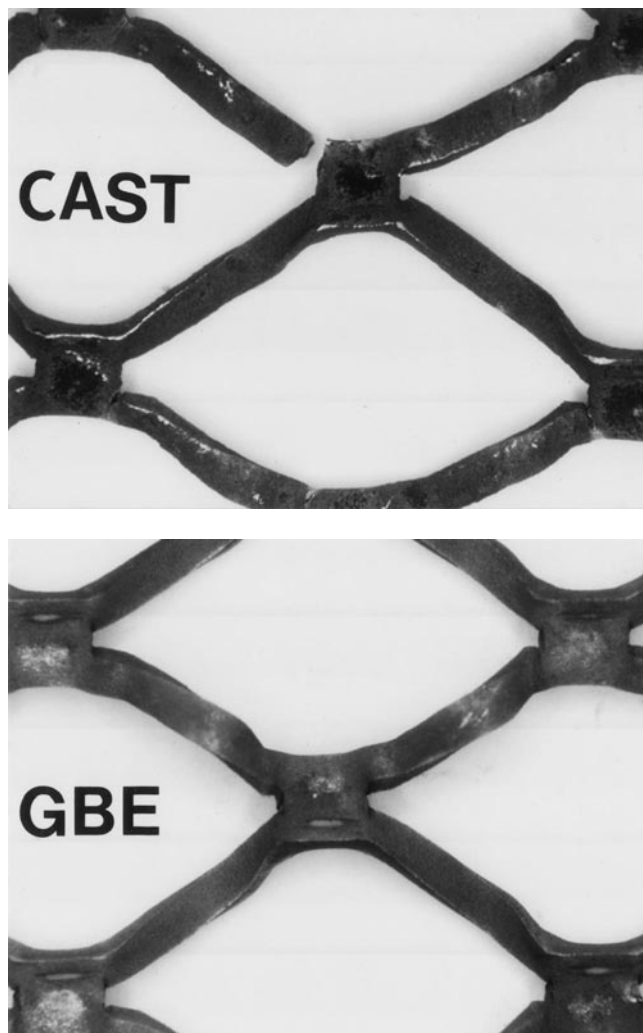


Fig. 13—Comparison in the extent of cracking observed in conventional cast ($F_{sp} = 13$ pct; $GS = 35 \mu\text{m}$) and GBE ($F_{sp} = 52$ pct, $GS = 15 \mu\text{m}$) PbSb grids after cycling tests (70 cycles at 2 cycles/day between 0 and 1.71 Vdc in 1.28 sg H_2SO_4).

The role of special boundaries in reducing susceptibility to age hardening is consistent with their propensity for minimizing the segregation and sensitization reported in numerous alloys (e.g., $\text{Ni}^{[9]}$ and $\text{Fe-Si}^{[28]}$). Age hardening can shorten the time available between casting and expansion where grids can be formed (expanded) with a minimum number of defects. These data suggest that introducing special boundaries in lead alloys may extend or eliminate this window, and in doing so, offer greater flexibility in material inventory control.

D. Modeling Grid Degradation

Figure 13 depicts the effect of increasing the frequency of low- Σ CSL boundaries in the PbSb from 13 pct (cast) to 52 pct (GBE) on the extent of cracking during cycling. Cycled PbSb grids were selected for illustrative purposes, as these alloys display relatively low general corrosion rates, facilitating as accurate a measurement of intergranular penetration as possible. During cycling, cracking is primarily confined to node areas where residual stresses

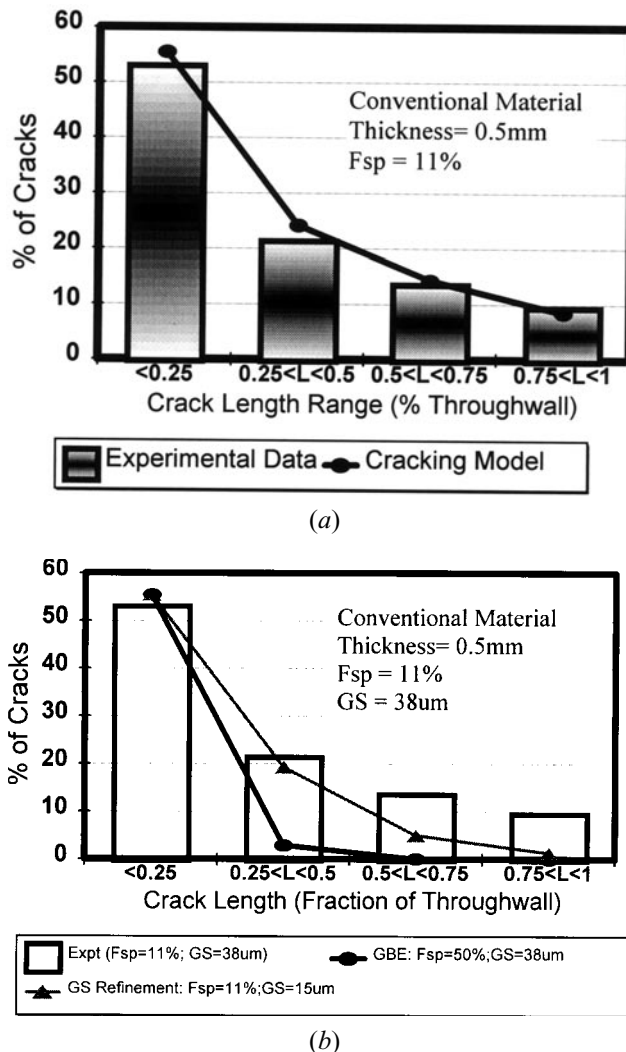


Fig. 14—(a) Comparison in the distribution of cracking observed in the conventional PbSb alloy ($F_{sp} = 11$ pct) with that predicted by the cracking model of Eqs. [1] and [2].^[15] (b) Relative effect of grain size refinement vs increasing the special boundary frequency on the crack distribution in the PbSb alloy projected from the cracking model of Eqs. [1] and [2]. Bar graph shows the experimental distribution of (a) for reference.

accumulated during expansion are the greatest, as shown in the macrograph of Figure 13. The depth distribution of cracking in conventional PbSb battery grids ($F_{sp} = 13$ pct; $GS = 35 \mu\text{m}$), as a fraction of the grid thickness (L) after 70 cycles, is compared in Figure 14(a), with the corresponding distribution *predicted* by the cracking model of Eqs. [1] and [2]. The cracking model accurately predicts the extent of attack observed. Figure 14(b) compares the predicted impact of increasing the frequency of special boundaries ($F_{sp} = 50$ pct; $GS = 38 \mu\text{m}$) or refining grain size ($F_{sp} = 11$ pct; $GS = 15 \mu\text{m}$) on the crack depth distribution observed in the cast material (bar graph). Increasing the frequency of low- Σ boundaries is shown to exhibit a greater efficacy in reducing cracking susceptibility than grain size refinement. In fact, according to Eqs. [1] and [2], grain sizes on the order of 4 to 5 μm would be necessary (although impractical) in conventional materials containing special grain boundary fractions of 10 to 12 pct, in order to achieve a similar resistance to that reflected in curve 1

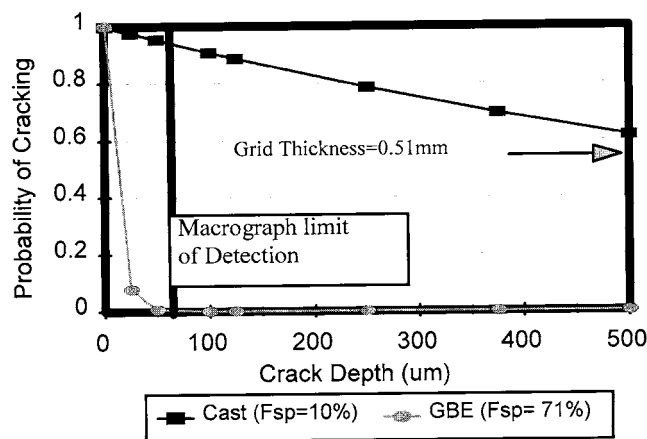


Fig. 15—Distribution of cracking in the GBE vs cast “Hi” Sn alloy predicted from the cracking model.

(GBE) solely on the basis of grain size refinement. Hence, even if growth arises predominantly from a cracking phenomenon, as suggested by Figure 10, the GBE approach can be expected to provide superior growth properties than would otherwise be practical by *traditional* grain size refinement techniques (such as quench-casting, nucleant additives, etc.).

Unfortunately, a similar analysis could not be undertaken for the GBE grids since cracking depths were insufficient to be reliably detected with the macroscopic technique employed. However, the absence of *detectable* macrocracking is consistent with the crack distributions predicted by the model. Specifically, at special boundary frequencies of 52 pct and grain sizes of 15 μm, the probability of observing cracks at depths of 0.063 (1/8 wall thickness) is <0.007 pct. In grids containing 100 nodes with four points/node that are susceptible to cracking, no significant crack penetration would be expected to be observed within the grid dimensions considered.

Predicting the extent of attack, however, is by no means confined to PbSb systems or cycling environments. The condition of the “Hi” Sn grids after static corrosion tests, shown in Figure 6, are also *qualitatively* consistent with predictions derived from the cracking model. The probability of crack propagation as a function of crack length for the GBE ($F_{sp} = 70.9$ pct; GS = 24 μm) and conventionally cast ($F_{sp} = 13$ pct; GS = 98 μm) material appears in Figure 15. Approximately 60 pct of all cracks developed in the *cast* material are predicted to breach the grid cross section, propagating to lengths greater than 0.51 mm. A depth of attack in which almost two-thirds of the nodes are compromised would be sufficient to jeopardize the structural integrity of the grid, leading to the overall condition depicted in Figure 5. On the other hand, the probability of observing through-wall cracking in the GBE grid is effectively nil, which accurately reflects the absence of through-wall cracking in the processed grids. In general, the correlation between the observed intergranular attack depth and that predicted by the cracking model further substantiates the position that growth phenomena arise from both cracking and creep mechanisms, rather than simply creep. While semiquantitative, these results also underscore the potent

effect of special boundaries in mitigating intergranular effects leading to battery grid deterioration.

IV. CONCLUSIONS

1. The frequency of low- Σ CSL grain boundaries can be enhanced in a wide variety of commercial PbCaSn and PbSb grid alloys from levels of approximately 10 pct in conventional (cast) material to values of 50 to 70 pct. Moreover, special boundaries present in the microstructure exhibit sufficient thermal stability to survive prolonged exposures to maximum battery operating temperatures (90 °C).
2. Increases in the frequency of special grain boundaries in lead alloys are accrued mostly from the evolution and interaction of twin boundaries, consistent with the Fullman-Fisher concept, as evidenced by the prevalence of twin variants (*i.e.*, $\Sigma 3^n$; $n = 1, 2, \text{ and } 3$) in the GBCD of suitably processed materials.
3. Increases in the frequency of special boundaries in PbCaSn alloys beyond 50 pct are accompanied by declines of 26 to 46 pct in weight loss and 41 to 72 pct in grid growth. Growth in PbCaSn alloys having a special boundary fraction in excess of 50 pct approach rates typically found in PbSb grids of similar thickness. This offers the potential for replacing traditional PbSb battery grids with PbCaSn alloys, even in high-cycle applications, to eliminate water loss and antimony plate-back effects in maintenance-free designs.
4. Increasing the frequency of special boundaries affects neither the yield nor tensile strength of the alloys. However, alloys containing high proportions of low- Σ CSL boundaries exhibit significantly improved ductility over conventionally cast material. Likewise, grid microstructures containing high frequencies of special boundaries appear less susceptible to age hardening, offering greater flexibility in inventory control and manufacturing.
5. Intergranular attack/cracking, responsible for weight loss and grid growth in these alloys, occurs preferentially along random boundaries (*i.e.*, $\Sigma > 29$) such that its distribution can be accurately predicted based upon the frequency of low- Σ CSL grain boundaries and grain size in the microstructure. The extent of grid growth exhibits a direct correlation to the frequency of special boundaries and the inverse of grain size, suggesting a significant contribution from cracking to the overall grid growth rate. This, coupled with the greater effect demonstrated for special boundaries in resisting cracking over conventional means such as grain size refinement, advocates a role for GBE in mitigating the intergranular effects responsible for battery grid deterioration.
6. Reduced weight loss and grid growth, obtained by altering the GBCD toward higher frequencies of low- Σ CSL boundaries, may also provide additional margins for minimizing grid thicknesses and/or reducing material costs.

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